# HOT WATER EXTRACTION OF BITUMEN FROM
# UTAH TAR SANDS

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## INTRODUCTION

The dramatic projections for the energy market in the next few years have forced applied researchers and process designers to consider energy sources other than petroleum; such as tar sands, oil shale and coal.  Physically tar sands consist of sand grains surrounded by a bituminous film  (Figure 1)· This bituminous coating, if properly separated from the sands, may certainly be used as feedstock for the production of fuels and petrochemicals.

Utah has 51 deposits of tar sands containing an estimated 25 billion barrels of bitumen in place, which is about 95% of the total mapped resources in the United States(1).  Although the extent of Utah tar sands is small in comparison to the large bitumen potential of Canadian tar sands, which amounts to approximately 900 billion barrels, Utah deposits do represent an appreciable potential when compared to the United States domestic petroleum and condensate production of 3.2 billion barrels of equivalent oil in 1974 and the United States crude oil imports of 1.3 billion barrels during the same year.  In spite of its significance, extraction and processing technology of Utah tar sands has not yet been developed.  Since noticeable differences in the chemical and physical properties between Canadian and Utah bitumens have been observed, the technology acquired over the last fifty years in Canada can not be applied to Utar tar sands directly; rather, a detailed investigation on Utah tar sands in required.

Currently, at the University of Utah, an ambitious research program on Utah tar sands is being conducted in order to obtain basic information concerning products characterization and process development.  Different aspects of interest such as mining,extraction, upgrading and characterization of the products are being studied.  The purpose of this paper is to summarize some of the advancements in the hot water extraction of bitumen from Utah tar sands and the characterization of this bitumen, specifically its viscosity.

## FUNDAMENTALS OF THE HOT WATER PROCESS

The Hot Water Process (HWP) was first described by Dr. K.A. Clark in 1923 (2,3) and it is currently being used on a commercial scale by Great Canadian Oil Sands Limited in Athabasca, Province of Alberta, Canada (4,5).  In this process, the displacement of the bitumen from the sands is achieved by wetting the surface of the sand grains with

an aqueous solution (Figure 2),  The aqueous solution contains a caustic
wetting agent, such as sodium hydroxide, sodium carbonate or sodium
silicate.  The resulting strong surface hydration forces operative
at the surface of the sand particles give rise to the displacement
of the bitumen by the aqueous phase.  The name of the process comes
from the fact that the system is operated at temperatures near the
boiling point of water.  Once the bitumen has been displaced and the
sand grains are free, the phases can be separated by froth flotation
based on the natural hydrophobicity exhibited by the free bituminous
droplets at moderate pH values.

The mechanism of bitumen displacement from the solid surface is
not yet well understood and, as a result, a useful theoretical frame-
work does not exist.  Most approaches have been based on an energy
balance for the system postulating that, in order for the bitumen to
be displaced, the total free energy of the system must decrease.
Thermodynamically, this can be expressed as (6,7):

$$dF = \Sigma\mu dn + \Sigma\phi dq + \Sigma\gamma dA < 0, \qquad\qquad 1)$$
$$\text{at constant temperature and volume}$$

where

$dF$ =  Helmholtz free energy change

$\Sigma\mu dn$ =  change in free energy due to chemical reaction

$\Sigma\phi dq$ =  change in free energy due to a change in surface charge

$\Sigma\gamma dA$ =  change in free energy due to a change in surface energy

Summations include all the phases and interfaces present in the system.
In the past, the term corresponding to chemical reaction and the one
corresponding to surface charge have been neglected.  In addition,
changes in interfacial area have often been neglected, which may be
acceptable in mineral flotation systems but not in oil displacement where
the variations in interfacial areas are significant.  Further, as
pointed out by Leja and Bowman (6), the magnitude of the electrical
work term in aqueous systems may be of the same order as that of the
surface work.  Consequently, it seems that neither the surface energy
term nor the surface charge term should be neglected in Equation 1.

There are several objections to this fundamental approach.  The
first one is related to the difficulties in obtaining reliable informa-
tion on solid-liquid interfacial tensions and also, the complexities
appearing from the estimation of the surface charge term in Equation 1.
The second objection is that, even if the above information is available,
the model only provides a qualitative description of the process which
cannot be successfully used for process control or design.  Finally,
the highly viscous nature of the bitumen in Utah tar sands may give
rise to kinetic barriers, in such a way that the equilibrium condition
predicted by Equation 1 may be unattainable in a reasonable period
of time.  Also, electrostatic barriers could be expected (6).

Consequently, a radically different approach is needed.  The applica-
tion of new concepts in the modeling of particulate processes, such
as Population Balance Models, which are phenomenological in nature,
may result in a better description of the system.

# EXPERIMENTAL

## Hot Water Extraction Tests

As stated before, due to the difference in physicochemical pro-
perties between Canadian and Utah tar sands, the optimum operating
conditions and the phase disengagement mechanism itself would be
expected to be different. Because of the high viscosity of the Utah
bitumen, a high shear, stirred tank reactor was selected for digestion
of the tar sand samples, and wetting agents were added to assist the
phase disengagement process.

A flowsheet of the process is presented in Figure 3. Mined tar
sand feed is extruded down to smaller pieces ( 3/8") and fed to a 1-
gallon, model 1-E-150-SFTN, stirred tank reactor, manufactured by
Bench Scale Equipment Co. The impeller for this reactor consists of
two pitched blade turbines, 4" OD, which can be easily exchanged with
several other types of turbines or propellers. Additional features
of this reactor are a torquemeter, a reflux/takeoff condenser, a temper-
ature control and heating system, a SCR speed controller and a tacho-
meter. In the reactor, the feed is contacted with the hot aqueous
solution and stirred, at constant temperature, for a specified digestion
time. Ideally, at the end of the digestion stage, the bitumen has
been displaced from the sand surface and can be separated from the
dispersed sand in a standard bench scale Denver flotation machine where
bitumen is floated with air. At this point in the research program,
no frothers or collectors have been added in the flotation stage. The
hydrophobic bitumen concentrate removed from the top of the flotation
cell would be sent to a refining plant. On the other hand, the hydro-
philic free sand grains sink to the bottom of the cell for discharge,
thickening and disposal. On occasions, relatively large lumps of non-
floatable bitumen are found with the sand tails. This material can be
recovered from the tails, simply by screening on a vibratory screen
(14 mesh). The scavenger concentrate so produced has a grade suffi-
ciently high to either by recycled or refined as is. In any event, a
scavenger is not obtained when digestion has been done efficiently.

## Analytical Techniques

Samples of the feed, concentrates and tailings obtained during
experimentation are analyzed to determine their composition with res-
pect to bitumen, sand and water. For this purpose, three Dean and
Stark assemblies (Figure 4) were set up according to the procedure
reported by the U.S. Bureau of Mines (8).

A weighed sample, contained in a double thickness cellulose ex-
traction thimble, is placed in the neck of a specially designed receiver
flask, held by four indentations. About 200 ml of reagent grade toluene
are added to the flask and heated to boiling. Toluene vapors dissolve
the bituminous materials in the sample and also, remove any trace of
water present. The vapors of the toluene - water mixture are trapped
by the condenser. Due to its higher specific gravity, water separates
from the condensate and is collected in the capillary tube,while the
toluene is refluxed. After a few hours (4-6), extraction reaches comple-
tion and the volume of water in the sample can be read from the graduated
capillary. The thimble is dried and weighed to determine the amount of
solids left, and the bitumen is calculated by difference, assuming the
density of the water is equal to unity. This analytical technique has
proved to have very good reproducibility, $\pm$ 0.1%.

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## Bitumen Characterization

The most appropriate way to characterize the raw bitumen for hot water processing is by its viscosity. The viscosity is an important property of the bitumen and the determination of its dependence on temperature and system composition will help to establish the optimum conditions for the separation. Furthermore, this fundamental property is of primary importance to insitu mining, recovery, upgrading and material handling processes. Process design will strongly depend upon the viscosity of the feed and products.

Samples of pure bitumen were prepared by dissolving the flotation concentrates obtained from HWP experiments with an excess of benzene, allowing the sand remaining in the concentrate to settle, transfering part of the liquid to another vessel, and finally,evaporating the benzene by heating the solution on a hot plate, for an extended period of time (10-15 hours).

The viscosity of Athabasca and Utah bitumens were determined with a rotational viscometer, Rotovisco. This instrument allows the operator to set the temperature of the sample as desired, adjust the angular velocity of the rotating bob and measure the torque necessary to maintain that velocity; so that, a flow curve (shear stress versus shear rate) can be obtained, based on 3 easily determined calibration constants.

<div align="center">RESULTS AND DISCUSSION</div>

## Hot Water Extraction

Preliminary extraction experiments were performed in order to establish the range of conditions under which the separation could be made. The main variables being considered in the Digestion and Flotation stages are listed in Table I.

<div align="center">TABLE I.   OPERATION VARIABLES CONTROLLING<br/>THE PERFORMANCE OF THE HWP</div>

| DIGESTION: | Discrete | Feed Source |
| | | Wetting Agents |
| | | Impeller and reactor design |
| | Continuous | Temperature |
| | | Percentage solids in the vessel |
| | | Digestion time |
| | | Wetting agents additions |
| | | Feed size distribution |
| | | Intensity of agitation (RPM) |
| FLOTATION: | Discrete: | Cell Design |
| | | Flotation Reagents |
| | Continuous | Percentage Solids |
| | | Intensity of Agitation |
| | | Temperature |
| | | Solution pH |
| | | Flotation reagents additions |

Owing to the large number of variables and the lack of background information on the subject, the effect of each individual variable on the overall performance could not be studied separately as this would require a very large number of experiments. Rather, experimental design

techniques in which the number of experiments is reduced to a minimum are being considered for application in combination with several optimization algorithms. With this approach, the main objectives are to determine the optimum experimental conditions for separation and to formulate a mathematical description of the system response in the region of the optimum. This sort of information, if obtained, will provide a solid basis for the development of theoretical and semi-theoretical models.

The excellence of the separation is quantified not only by the grades of the concentrates and the recovery of the different components but also by the coefficient of separation (CS), which is defined as the fraction of the feed material which undergoes a perfect separation, while the rest of the feed is distributed unchanged into the respective product streams(9). In terms of recoveries, it can be shown that the CS is equal to the difference between the recovery of bitumen in the concentrate and the recovery of sand in the same concentrate.

So far, HWP extraction tests have been performed with samples from three different Utar tar sand deposits: Asphalt Ridge, P.R. Spring and Sunnyside. Scanning electron photomicrographs of these samples are shown in Figure 1. Satisfactory results were obtained only with the first two samples, namely, Asphalt Ridge and P.R. Spring which exhibited a fairly similar behavior. Typical results are presented in Table II. Unexpectedly high coefficients of separation and recoveries of bitumen in the concentrate were obtained under these conditions. These high coefficients of separation are indicative of an excellent separation and suggest that development of a HWP for Utah tar sands may be possible.

TABLE II. HOT WATER EXTRACTION TESTS FOR
ASPHALT RIDGE AND P.R. SPRING SAMPLES

EXPERIMENTAL CONDITIONS

Digestion: Wetting Agent addition: 0.2 (g sodium silicate/g tar sands
Temperature: $200^{\circ}$F
Percentage Solids: 67%, by weight tar sands
Digestion time: 15 min; RPM = 1000
Flotation: Percentage Solids: 20%, by weight tar sands
RPM = 1200
Temperature = $15^{\circ}$C

ASPHALT RIDGE

|  | Weights % | Grade,% Tar | Sand | Recoveries,% Tar | Sand |
|---|---|---|---|---|---|
| Conc. | 14.68 | 83.74 | 16.26 | 97.15 | 2.72 |
| Tail | 85.83 | .42 | 99.58 | 2.85 | 97.28 |
| Feed | 100.00 | 12.65 | 87.86 | 100.00 | 100.00 |

P.R. SPRING

|  | Weights % | Grade,% Tar | Sand | Recoveries,% Tar | Sand |
|---|---|---|---|---|---|
| Conc. | 20.38 | 70.50 | 29.50 | 99.12 | 7.03 |
| Tail | 79.62 | .16 | 99.84 | .88 | 92.97 |
| Feed | 100.00 | 14.50 | 85.50 | 100.00 | 100.00 |

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However, there is a negative aspect related to the results pre-
sented in Table II in that, an excessive amount of sodium silicate
(20% by weight of the tar sand feed) was added as a wetting agent.
When the sodium silicate addition was reduced to 5%, the digested bitu-
men became very sticky and a much lower concentrate grade of 53.5% tar
was obtained. Under these conditions the recovery was 89%. The
inferior response at low sodium silicate additions may be related to
the pH of the digested pulp, whose critical role in bitumen displace-
ment has been recognized elsewhere (4,6,10).

Tar sands in general are slightly acidic so that they will consume
base when contacted with a caustic solution. Consequently, titration
curves of Utah tar sands with sodium silicate and other caustic solu-
tions ought to be determined in order to be able to predict the pulp
pH during digestion. Equilibrium pH values ranging from 8.0 to 8.5
proved to be successful in processing Athabasca tar sands (4), but
corresponding evidence for Utah tar sands has not been reported.

Samples from Sunnyside do not seem to be amenable for Hot Water
extraction. These results can be explained based on the low bitumen
content of these samples (less than 8%, by weight) which gives a brittle
nature to the feed material. In fact, the samples obtained could be
easily ground to -65 mesh or finer in a conventional tumbling mill.
Such was not the case with samples from Asphalt Ridge and P.R. Spring
which could only be reduced in size to a limited extent by extrusion.
Also, as can be observed in Figure 1, there is a remarkable constitu-
tional difference between low and high grade tar sands. Unlike the
Sunnyside sample (Figure 1c), Asphalt Ridge and P.R. Spring samples
(Figure 1a and 1b, respectively) exhibit a continuous bituminous matrix
surrounding the sand grains. With such samples shear forces can be
transferred to the bitumen-solid interface through the continuous matrix.
As a result, deformations occur at the interface which allow for the
aqueous solution to advance to the interface and wet the sand grains.
In other words, a high shear stress field helps to destroy kinetic
barriers such as those mentioned before at the end of the section on
Fundamentals. On the other hand, the bitumen content of Sunnyside
samples is low and is not present as a continuous matrix; hence the
tar sand particles are free flowing inside the reaction vessel. In
such cases, it appears that shear stress cannot be transferred to the
bitumen-solid interface for phase disengagement. Alternative processes
such as thermocracking in fluidized bed reactors seem to be more appro-
priate to process the low grade tar sands.

In most of the experiments, the digestion time was 15 min. Separa-
tion was not significantly improved by increased digestion times
indicating that residence times shorter than 15 minutes may be acceptable.

Bitumen Characterization

The flow properties of a fluid are completely described by the
relationship between the shear stress applied to a fluid element and
the rate at which the element is deformed as a result of the applied
stress (shear rate). This relationship is characteristic of the
fluid and is referred as its flow curve. Usually, flow curves are
determined experimentally and the collected information is then
correlated on the basis of some semi-theoretical models, such as the
well known Newton's law of viscosity. A Newtonian fluid is such that
its viscosity, defined as the proportionality constant between the

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applied shear stress and the resulting shear rate, is constant, equal to the slope of the flow curve.

Flow curves for Athabasca and Asphalt Ridge bitumens are shown in Figures 5 and 6 for various temperatures. The essentially linear response for both samples indicates that both bitumens behave as Newtonian fluids, i.e. the viscosity is independent of the rate of shear and can be calculated from the slope of the lines, at a given temperature. Perhaps of more practical significance is the fact that the viscosity of the Utah bitumen is about two orders of magnitude greater than the viscosity of the Canadian bitumen in the temperature range studied, as shown by the plots presented in Figure 7. This accounts for the fact that the Athabasca tar sands can be digested in a simple tumbling mill, while the Utah tar sands seem to require intense shear conditions. The measured temperature dependence of both bitumens follows very closely a functional relationship of the type:

$$\mu = Ae^{B/T}$$

where

$\mu$ = viscosity, poises

T = temperature, $^{o}$K

A, B = empirical constants

In general, this type of temperature dependance is obtained for Newtonian fluids. Further, viscosity measurements of Athabasca bitumen agree well with data reported in the literature (4).

An apparent activation energy on the order of 27 (kcal/mole) was calculated for Utah bitumen from the data in Figure 7a, indicative of the fact that momentum transfer is accompanied by rather significant structural transformations.

Future studies on the effect of organic solvents on the viscosity of bitumen is contemplated as a part of this research program.

## SUMMARY AND CONCLUSIONS

Preliminary results indicate that effective disengagement and separation of bitumen from high grade Utah tar sands (12%,by weight bitumen) can be achieved by a hot water process, involving the addition of wetting agents, digestion under high shear conditions, and final separation by froth flotation. Coefficients of separation as high as 0.95 have been realized for these high grade systems. On the contrary, effective separation of low grade Utah tar sands (less than 8%, by weight bitumen) has not been achieved.

The processing technique described in this article differs signi-ficantly from the one used in processing Canadian tar sands, mainly because of a considerable difference in the viscosity of the two bitu-mens. Experimental data have established that Utah bitumen, which is shown to behave as a Newtonian fluid, is at least two orders of magni-tude more viscous than Athabasca bitumen.

Thus far in the research program, the following preliminary con-clusions have been obtained:
1. Effective separations by HWP can be attained for high grade tar sands.

2. Rather large additions of alkaline wetting agents are
      required for effective separation.
   3. For the experimental conditions reported, satisfactory
      phase disengagement is achieveable with digestion times of
      15 min or less.

## ACKNOWLEDGEMENTS

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a. ASPHALT RIDGE
   Bitumen Content: 13%, by weight

b. P.R. SPRING
   Bitumen Content: 12%, by weight
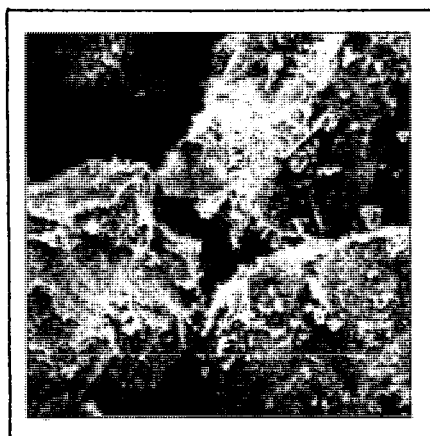
c. SUNNYSIDE
   Bitumen Content: 8%, by weight

Figure 1. Scanning Electron Photomicrographs of Utah
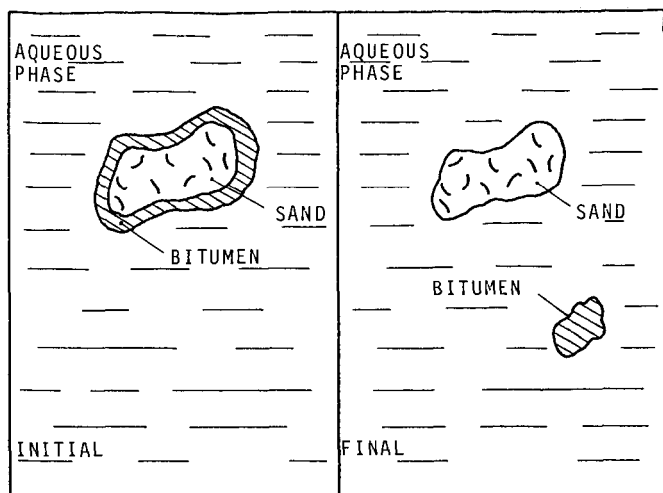          Tar Sand Samples.  Magnification: 200X.
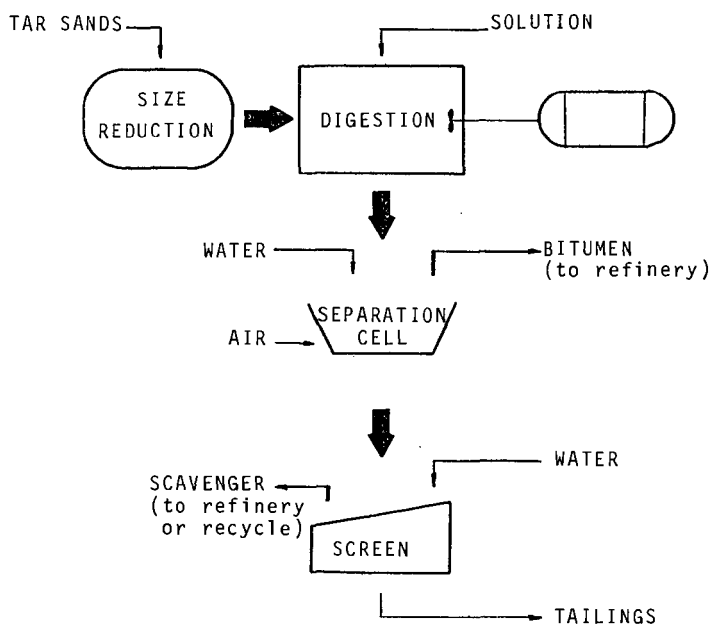
Figure 2. HOT WATER PROCESS. Bitumen Displacement.



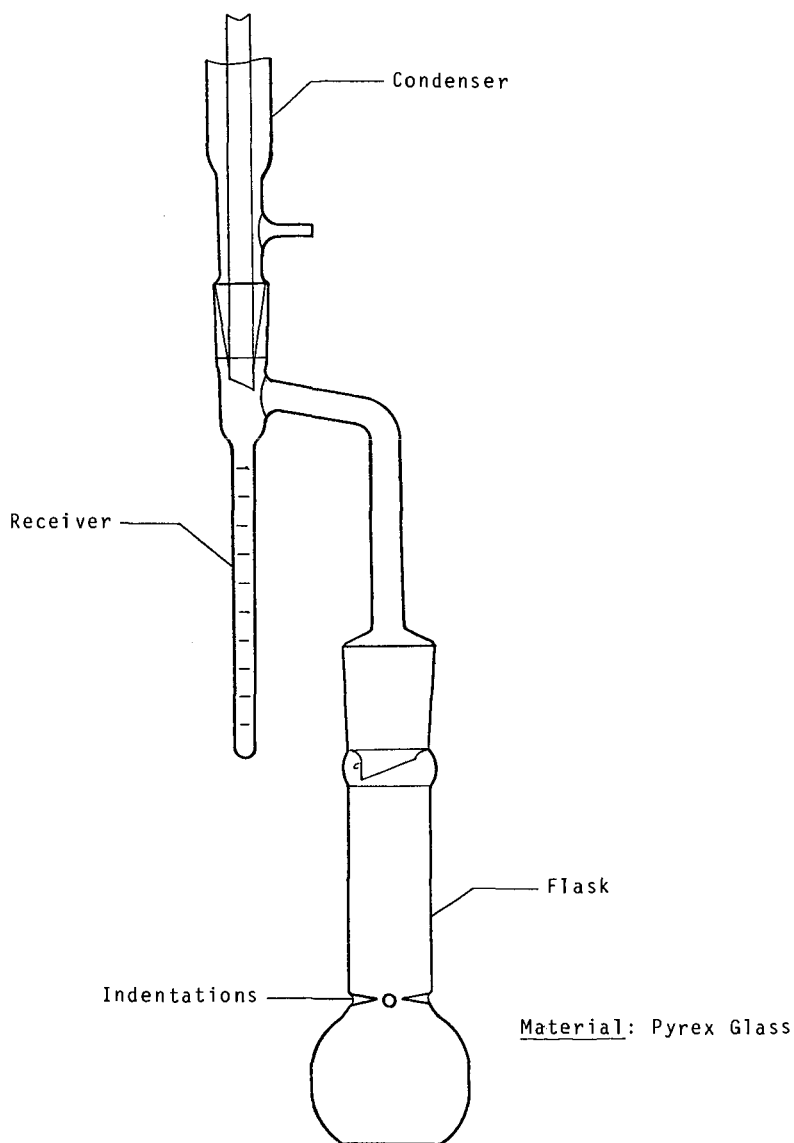Figure 3. HOT WATER EXTRACTION PROCESS. Flowsheet.

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Condenser

Receiver

Flask

Indentations

Material: Pyrex Glass

Figure 4.   Dean & Stark Tube Assembly.

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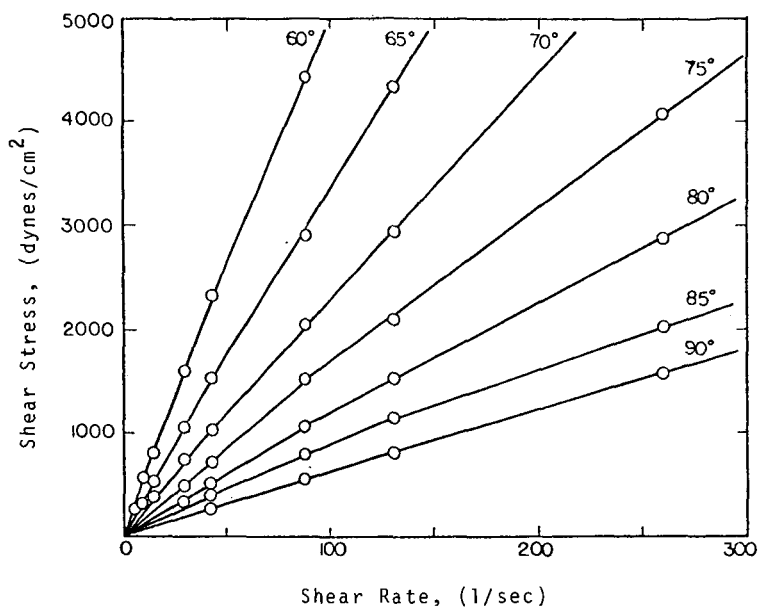
Shear Rate, (1/sec)
Figure 5. Flow Curves of Athabasca Bitumen.
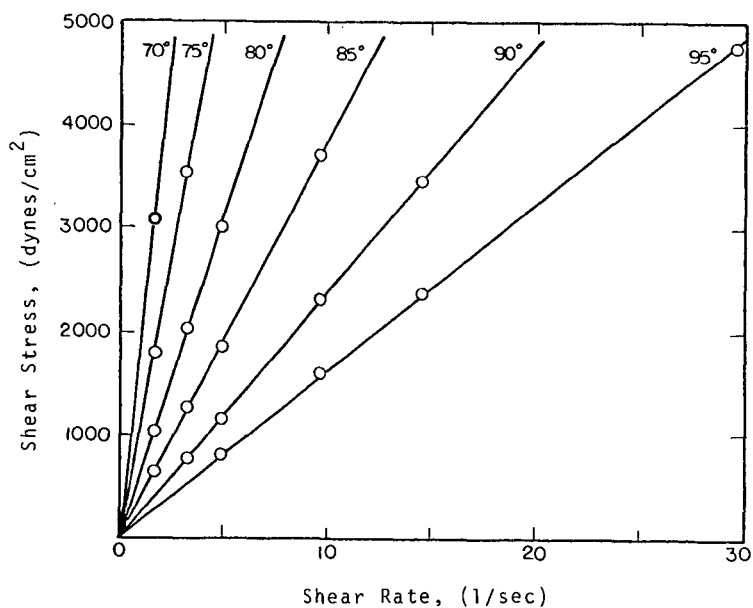


Shear Rate, (1/sec)
Figure 6.  Flow Curves of Asphalt Ridge Bitumen.

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a. Asphalt Ridge Bitumen
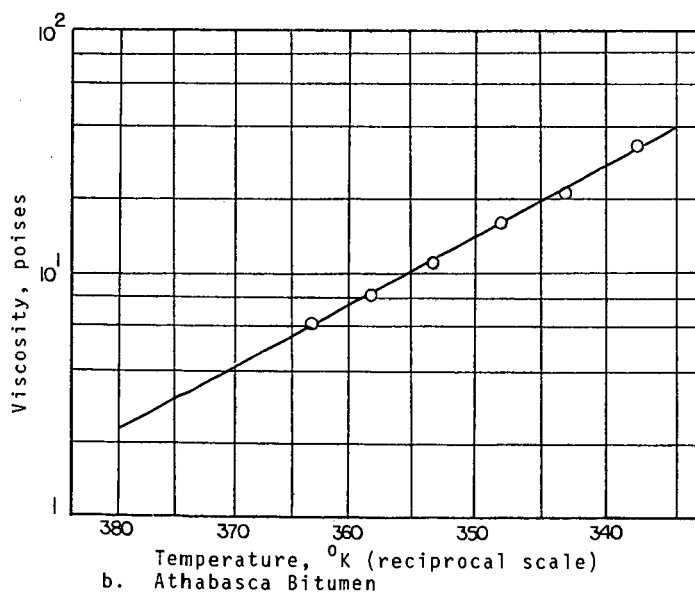


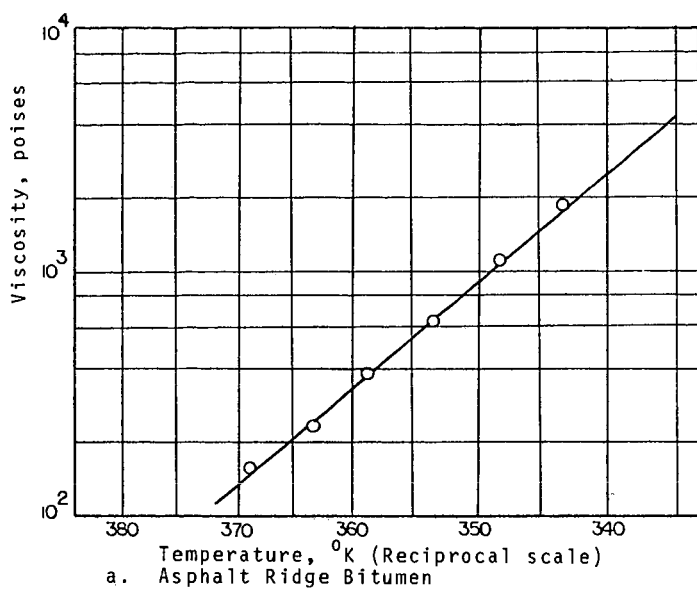b. Athabasca Bitumen

Figure 7.    Effect of Temperature on the Viscosity
            of Asphalt Ridge and Athabasca Bitumens.